Local Disorder and Neutron Scattering: From Catalysts to High-Temperature Superconductors

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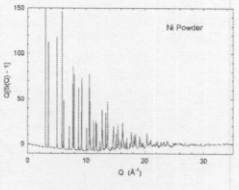
To get started

- *Why study the structure ?*
  - *To understand the structural underpinning of the properties, and gain insights on improving them. ⇒ Knowing the crystal structure may not be enough, since properties of real materials are often controlled by* ***defects*** *and other* ***deviations from perfect lattice.***
- *Why neutrons ?*
  - *Light elements, such as* ***oxygen****, are better seen by neutrons.*

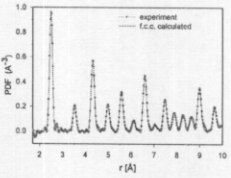
Deviation from periodicity

- *Periodic structure* ⇒ ***Bragg peaks***
- *Non-periodic structure* ⇒ ***Diffuse scattering***
- *Direct measurement of diffuse scattering*
  - *Has to be measured over large Q space*
  - *Diffuse peaks tell correlations, but not what they are*
- ***Atomic pair-density function*** *(PDF):*
  - *Fourier-transform of the total scattering, including Bragg peaks and diffuse scattering.*
  - *Describes periodic as well as non-periodic structure; no assumption of periodicity made.*
  - *Has long been used in the study of liquids and glasses, applicable to crystalline materials because of the advent in high-energy probe sources.*
  - ***Underneath the Bragg peaks****, T. Egami and S. J. L. Billinge*

Local Structure by Pulsed Neutron Atomic Pair-Density Function (PDF)



$\Rightarrow$ FT



- Distribution of distances between atoms, can describe local structural deviations. The use of pulsed neutron source critical (high energy neutron to cover large Q space).

PDF Measurement with Crystals

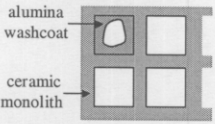
- *Neutrons:*
  - *IPNS (SEPD, GPPD, GLAD)*
  - *LANSCE (HIPD, NPD)*
  - *ISIS (GEM, POLARIS, SANDAL)*
  - *KENS (Sirius, Vega)*
  - *ILL (Hot Source, D-4)*
- *X-rays:*
  - *NSLS (X-7A)*
  - *CHESS*
  - *APS (SRI-CAT, BESSRC-CAT)*

Complex Oxides: Examples

- *Catalyst support in automotive exhaust control system (three-way catalytic converter).*
- *Manganites that show colossal magnetoresistivity (CMR).*
- *High-T_C superconducting (HTSC) cuprates.*

Motivation

- **Three-Way Catalyst**



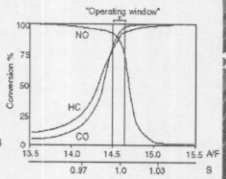
- Oxides: CeO_2, ZrO_2, La_2O_3
- Catalytic Metals: Rh, Pd, Pt

- **simultaneous oxidation**

$$CO, HC \longrightarrow CO_2$$

- **and reduction**

$$NO_X \longrightarrow N_2$$



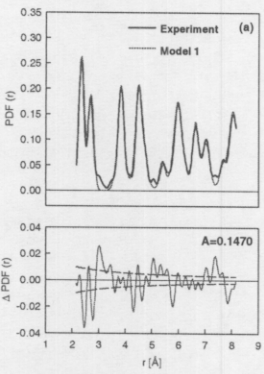
Ceria: Oxygen Storage

fuel rich: $CO + CeO_2 \longrightarrow CO_2 + Ce_2O_3$

fuel lean: $Ce_2O_3 + O_2 \longrightarrow CeO_2$

Ceria as catalyst support oxide

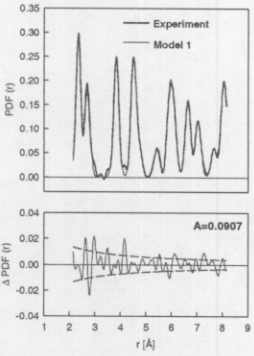
- *Ease of valence change, $Ce^{+4} \leftrightarrow Ce^{+3}$, provides oxygen storage capacity (OSC).*
- *OSC deteriorates after long use or high temperature treatment.*
- *Grain coarsening and loss of surface area is not the primary cause.*
- *Mixing with zirconia (ZrO_2) is known to prolong the lifetime, but mechanism is unknown.*



The PDF of nano-powder ceria compared to the PDF calculated for the perfect crystal structure.

Difference PDF (below) shows significant disagreement, in addition to noise of which r.m.s. is shown by dashed lines.

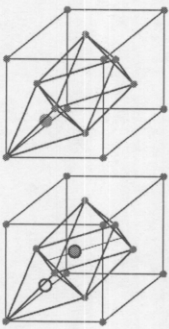
E. Mamontov and T. Egami, J. Phys. Chem. Solids, 61, 1345 (2000)

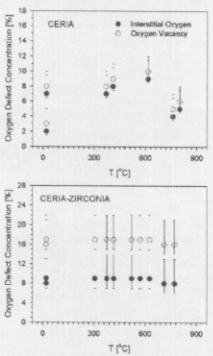


PDF of nano-powder ceria compared to the PDF calculated for ***the model with interstitial oxygen defects*** *showing much better agreement. The difference is essentially due to noise. The results were confirmed by the Rietveld method.*

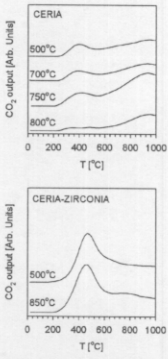
Interstitial Oxygen Model

- *Ce ions form f.c.c. sublattice.*
- *Regular site for oxygen is the tetrahedral site of f.c.c.*
- *Interstitial site is the octahedral site of f.c.c. which is more spacious.*
- *When a reduced sample is oxidized at a low temperature oxygen goes into the octahedral site.*





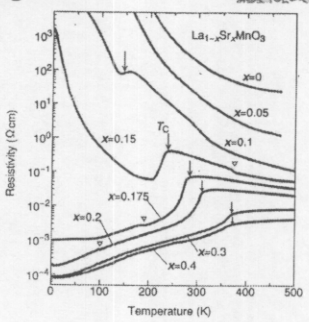
The concentration of oxygen defects (vacancies and interstitials) as a function of annealing temperature, for pure ceria (above) and for ceria/zirconia solution 70/30 (below). Zirconia keeps ceria reduced, and prolongs the life-time of ceria since it stabilizes the defects.



The neutron results agree perfectly with the TPD results, giving strong evidence that the oxygen defects provide the OSC.

Polarons in colossal magnetoresistive manganites

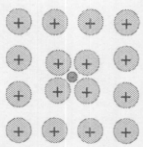
- *Metal-insulator transition (MIT) concomitant with ferromagnetic transition.*
- *MIT induced by applied magnetic field.*
- *Large negative change in resistance, up to $\rho(0)/\rho(H) = 10^4$.*



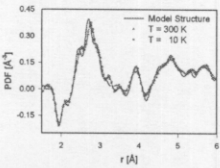
A. Urushibara *et al.*, Phys. Rev. B **51**, 14103 (1995).

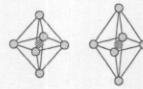
Polarons

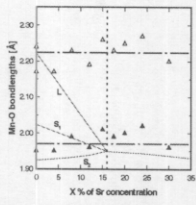
- *Why charges are localized up to as much as 17 %?*
- *They form spin-lattice* ***polarons****.*
- *Stability of the polaron is the key: Marginal stability produces the CMR effect.*



Local structure of $La_{1-x}Sr_xMnO_3$



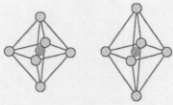


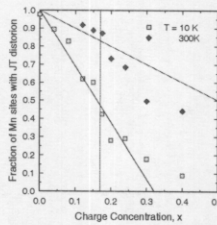


- *PDF of undoped sample (above).*
- *Doping kills the JT distortion in the crystal structure, but locally distortion remains (right).*

D. Louca *et al. Phys. Rev. B* **56,** R8475 (1997)

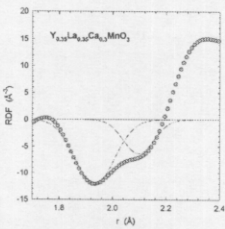
Local suppression of the JT distortion: Anti-JT polaron formation

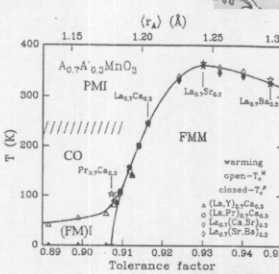




- *JT distortion locally suppressed due to polaron formation.*
- *Single site polaron at RT.*
- *Three site polaron at 10 K.*
- *Local JT distortions survive in the metallic phase.*

Ionic Size Effect





- *Local JT distortion and polaron formation in spite of high charge density (Louca and Egami, PRB 2001)*

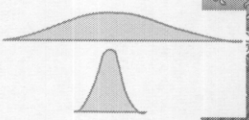
H. Y. Hwang, et al. PRL 75, 914 (1995)

Competing forces

- *Localization forces:*
  - *Electron-lattice coupling*
  - *Spin correlation*
- *Delocalization forces:*
  - *Electron kinetic energy*
  - *Elastic energy*
- *Balance:*

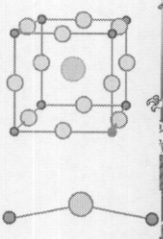
$$\lambda = \frac{g^2}{tK\langle \cos\theta/2 \rangle}$$

  - *g : Electron-phonon coupling*
  - *t : Electron hopping*
  - *K : Elastic constant*
  - *<cosθ/2> : Magnetic correlation*



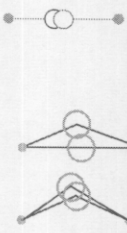
Ionic Size Effect

- *Small A ion ⇒ polaron stable; insulating.*
- *Large A ion ⇒ polaron unstable; metallic.*
- *M-O-M bond bending ⇒ reduced t.*
- *But this effect is only 2-3 %.*



Long-Range Stress Field

- *If the M-O-M bond is **straight** shortening one M-O bond produces tensile stress on the other, resulting in a **long-range stress field**.*
- *If the M-O-M bond is **buckled** shortening of one M-O bond can be **accommodated locally** without producing the long-range stress field.*
- *Difference in the driving force is a **factor of two**.*



Local Structure of HTSC Cuprates

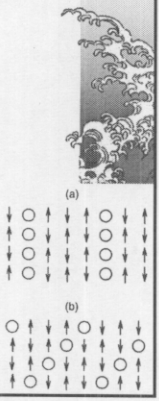
- *General assumption:*
  - *HTSC is a purely electronic phenomenon due to spin correlations.*
  - *HTSC cuprates are basically spatially homogeneous.*
  - *Observed inhomogeneity is related to defects, and thus unimportant.*

Something Fishy.....

- *Magnetic interaction, J, is comparable in magnitude (~150 meV) to phonon energy (~80 meV).*
- *Magnetic correlation diminishes as T_C is increased with doping.*
- *All of the HTSC cuprates have a large Debye-Waller factor (apparent phonon amplitude).*
- *K. Alex Müller discovered it with the dynamic Jahn-Teller interaction in mind.*
- *No theory on electron-phonon coupling in strongly correlated electron systems.*

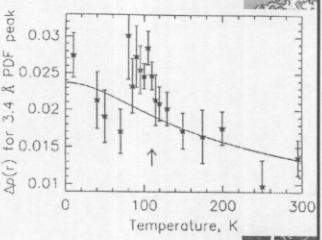
Actually.....

- *A large body of literature suggest local lattice distortion and lattice effects, including charge segregation and anomalies at T_C (e.g. T. Egami and S. J. L. Billinge, in* Physical Properties of High Temperature Superconductors V, *ed. D. Ginsberg (World Scientific, Singapore, 1996) p. 265).*
- *Electronic theories suggest spatial spin-charge separation (not only holon-spinon separation).*
- *Spin-charge stripes were observed (in non-superconducting LSCO with Nd).*
- *Magnetic theories never explained T_C over 100 K.*



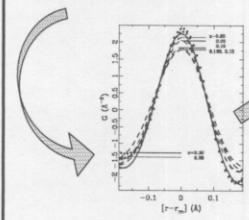
Local structural fluctuations in HTSC

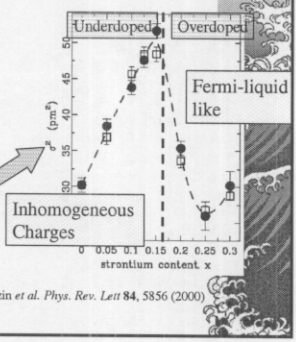
- *Pulsed neutron PDF peak at 3.4 A of $Tl_2Ba_2CaCu_2O_8$ due to O(in-plane)-O(apical) correlation suggesting critical slowdown at T_c of either the apical oxygen or the out-of-plane mode of the in-plane oxygen (PRL 64, 2414 (1990)).*



Evidence for Charge inhomogeneities: $La_{2-x}A_xCuO_4$ (A=Sr,Ba)

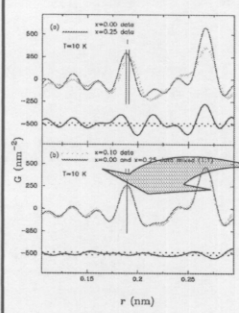
- *In-plane Cu-O PDF peak width broadens with doping (then sharpens)*



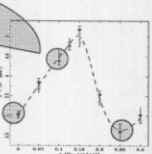


Bozin *et al. Phys. Rev. Lett* **84**, 5856 (2000)

Nature of the distortion



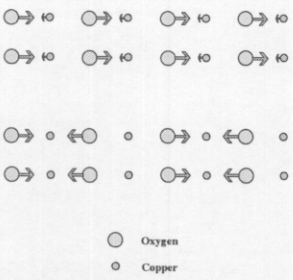
- *Broad peak in the underdoped data well explained as a mixture of long and short bonds from heavily doped and undoped material*
- *Bond length difference is ~0.02Å*



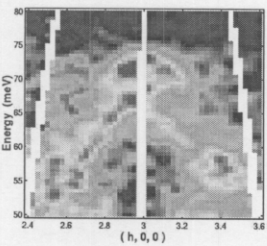
Bozin *et al. Phys. Rev. Lett* **84**, 5856 (2000)

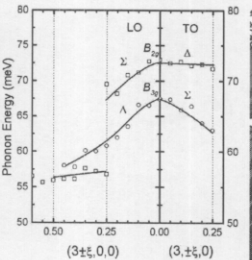
High-Energy LO Phonons

- *Cu-O bond-stretching modes:*



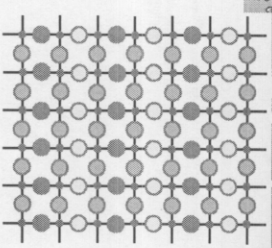
Cu-O Bond-stretching Mode, T = 110K
MAPS (ISIS)





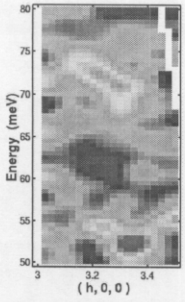
Spin-charge stripes with 2a periodicity

- *Related to formation of local spin-singlet; quantum stripes.*
- *Dynamic (~ 4 meV) and short-range (8 × 20 Å).*
- *Vibronic resonance with the zone-boundary LO phonon.*

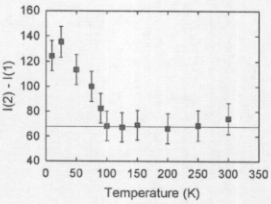


R. J. McQueeney et al., *PRL, 82, 628 (1999)*

I(7 K) – I(110 K)



At h = 0.25, I(51 – 55 meV) – I(56 – 68 meV)



Conclusions

- *Local structural distortions ubiquitous in complex oxides; probably in all complex materials.*
- *Understanding their role in determining the properties is an important subject of materials science.*
- *Neutron scattering will play a major role in this study.*